

# Molecular Structure Determined by Gas Electron Diffraction at High Temperature. Antimony Trifluoride

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The interatomic distances and the mean amplitudes for  $\text{SbF}_3$  have been determined by the sector-microphotometer method of gas electron diffraction to be  $r_g(\text{Sb-F}) = 1.876 \pm 0.005$  Å,  $r_g(\text{F} \cdots \text{F}) = 2.74 \pm 0.03$  Å,  $l(\text{Sb-F}) = 0.066 \pm 0.007$  Å,  $l(\text{F} \cdots \text{F}) = 0.16 \pm 0.04$  Å. The valence angle for  $\text{SbF}_3$ ,  $(\angle \text{F-Sb-F}) = 94.5 \pm 1.8^\circ$  is found to agree well with the proposal of Morino et. al. The first cutoff point due to the phase shift of electron waves scattered by  $\text{SbF}_3$  is observed to be about 63 in  $q$ -value.

## Introduction

The molecular structure of antimony trifluoride ( $\text{SbF}_3$ ) was first reported to be  $r(\text{Sb-F}) = 2.03$  Å and the valence angle  $\theta$  ( $\angle \text{FSbF}$ ) =  $88^\circ$  by A. Bystron and A. Westgren,<sup>1)</sup> but their results were from the X-ray diffraction in solid state. However, no information has been reported concerning the molecular structure of this molecule by the sector-microphotometer method of gas electron diffraction. Moreover, it is difficult to determine the molecular parameter precisely, because no available knowledge on infrared spectra of  $\text{SbF}_3$  has been given in literatures. In the case of the tetratomic trigonal pyramidal molecule ( $C_{3v}$  symmetry), there are six potential constants in the general quadratic potential function expressed in the usual distance and angle in terms of the internal coordinates. The four observed infrared fundamental frequencies (two of species  $A$ , and two of species  $E$ ) alone are insufficient for determining six potential constants. The  $E$  species of the factored secular determinant may be completely specified with the two  $\nu(E)$  vibration frequen-

cies and one Coriolis zeta constant,  $\zeta$ , determined experimentally by an analysis of the band envelope of the infrared spectra. The centrifugal distortion coefficients  $D_j$  and  $D_{jk}$  from microwave spectroscopy provide sufficient information for solving the force constant problem of the totally symmetric  $A$  species of the secular determinant.

Recently, Matsumura and Takeo<sup>2)</sup> obtained the centrifugal distortion constants,  $D_j$  and  $D_{jk}$ , as well as the rotational constants,  $B_0$ . The molecular structure derived from the observed rotational constants gives the most accurate results in many cases, but it includes the effect of the interaction of the vibration and rotation. On the other hand, the interatomic distances obtained from gas electron diffraction method are the thermal averages of instantaneous interatomic distances. So the mean amplitude of the interatomic distances provides another route, which gives useful information to fill up the lack of data for the evaluations of the six quadratic potential functions.

One of the purposes of the present work is to determine the molecular structure of  $\text{SbF}_3$  and find its quadratic potential constants, and the other is to obtain information of the scattering phenomena about that

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molecule which has atoms greatly differing in atomic number from other atoms. The phase shifts of the scattered electron waves calculated by Bonham and Ukaji<sup>3)</sup> and Kimura and Konaka<sup>4)</sup> are tested for  $\text{SbF}_3$ .

### Experimental

A sample of commercial antimony trifluoride ( $\text{SbF}_3$ ), 98% in purity, was sublimated three times under reduced pressure. Since  $\text{SbF}_3$  is strongly hygroscopic, it was treated so carefully that it might become almost completely free from moisture in all circumstances. A piece of purified sample was placed in an oven having a high temperature nozzle which had been described in the previous paper.<sup>5)</sup> For the purpose of taking photographs, the sample was heated to about 200°C in the oven in order to attain a sufficient vapor pressure, while the nozzle heated to about 400°C to prevent the condensation of the sample gas on the nozzle path.

Electron diffraction photographs were taken with an apparatus equipped with a  $r^3$  sector at a camera distance of  $10.702 \pm 0.004$  cm. The electron wave length, 0.0569<sub>5</sub> Å, was calibrated with the diffraction pattern of a gold foil. The pressure in the apparatus was about  $0.5 \times 10^{-4}$  Torr during photographic exposure. Photographs were recorded on Fuji Process Hard plates with exposure times ranging from about 1.0 to 1.5 min., and were developed at 20°C for 5 min. with ED-131 developer diluted twice. Several of photographs ranging from 0.2 to 0.4 in optical density were obtained, and the range of the scattering angle measured was from 20 to 100 in  $q$ -value.

### Analysis

The interatomic distances and their root-

mean-square amplitudes of  $\text{SbF}_3$  in gaseous state were determined from the diffraction photographs by a procedure similar to that usually adopted.<sup>6)</sup> The final results were obtained by means of a least-squares analysis of the molecular intensity curves,  $qM(q)$ . All of the calculations were carried out by using the HITAC 5020 computer.

**Molecular Intensity.** Six of the photographic plates were selected for analysis. They were scanned while being rotated rapidly around the center of the pattern across the diameter of the diffraction pattern with a microphotometer. In order to record the fine details of the photographs, transmittancy range corresponding to the undulations of the curve was magnified to about five times of the original scale by utilizing an amplifier built in the photometer. The magnification ratio was determined by a least-squares fit between the total scattering intensity of the molecule of the magnified curves and that of the original scale.

The photometer curves of the magnified and original scales were measured at intervals of  $q=1$ ; a value taken from one side of a curve was combined with the corresponding value from the other side, and an average was taken from point by point. The distance,  $\pi(q)$ , on the abscissa of a photometric curve corresponding to the scattering angle was calculated by using the value of  $L\lambda$ , which was obtained as  $L\lambda_g$  from a diffraction pattern of gold foil corrected by the method just described by the previous work.<sup>7-9)</sup> A linear relation between the optical density and the intensity of the scattering electron was assumed,<sup>8)</sup> because the optical densities of all the photographic plates for analysis were less than 0.4.

After the intensity curve had been corrected for the deficiency of the sector opening, it was divided by a levelling func-

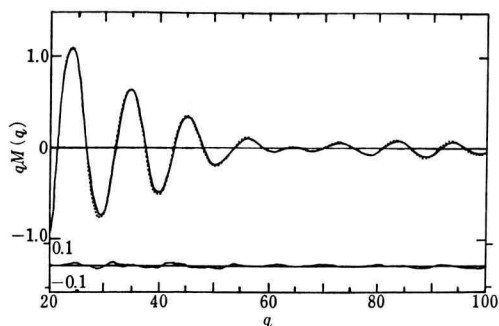


Fig. 1. The best fit of the molecular intensity curve represented by plotting the molecular scattering intensity  $qM(q)$  as ordinates versus the scattering angle given by  $q$ -value as abscissae. The upper full line shows the calculated  $qM(q)^{theo}$ , and the dotted one shows the observed  $qM(q)^{obs}$ . The lower curve gives the difference between them, i. e.,  $[qM(q)^{theo} - qM(q)^{obs}]$ .

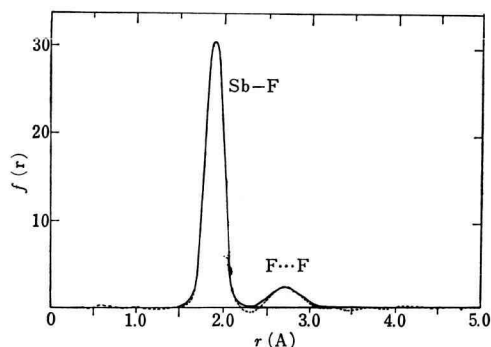


Fig. 2. Radial distribution curve  $f(r)$  calculated by the best fit molecular intensity. The full line is the calculated curve and the dotted curve is the observed one.

tion,  $f(q)$ , in order to obtain a levelled intensity curve,  $I_T(q)$ , which facilitated the drawing of a background line,  $I_B(q)$ . The  $f(q)$  function was derived by a least-squares fit of the intensity curve to a quadratic function. The most probable background line was obtained after two cycles of procedure of redrawing the line according to the non-negativity criterion<sup>10)</sup> with respect to the radial distribution curve  $f(r)$ , in which only two peaks were observed, one peak

showing the distance of Sb-F and the other that of F...F in Fig. 2. The artificial damping factor was so chosen as to reduce the molecular intensity to one-tenth of the original one at  $q=100$ .

$$qM(q) = q [I_T(q) - I_B(q)] / I_B(q) \quad (1)$$

**Phase Shift.** In order to obtain a correct theoretical molecular scattering intensity, the use of the complex atomic scattering factors of Ibers and Hoerni,<sup>11)</sup> instead of the first Born scattering factors, is necessary for the interpretation of the electron diffraction pattern of SbF<sub>3</sub>, which contains both heavy (e.g., Sb) and light (e.g., F) atoms. The effect of the phase angle difference of the atomic scattering factors, the so called phase-shift, had already been pointed out by Schomaker and Gluber.<sup>12)</sup> Numerous efforts in this connection have been made theoretically and experimentally by many workers.<sup>13-19)</sup>

According to the kinematical theory of electron scattering the reduced molecular intensity curve is given as;<sup>3)</sup>

$$M(s) = \frac{\sum'_{ij} |f_e(s)_i| |f_e(s)_j|}{\sum_k [|f_e(s)_k|^2 + S_k(s)/s^4]} \cos [\eta_i(s) - \eta_j(s)] \int_0^\infty P_{ij}(s) \frac{\sin sr}{sr} dr \quad (2)$$

where terms  $f_e(s)$  are the complex electron scattering factors,  $S_k(s)$  is the inelastic scattering for  $k$ -th atom,  $P_{ij}$  is the probability that the  $i$  and  $j$ -th atom pair will be separated by a distance  $r$  and  $s$  is the electron scattering variable, and is given by  $s = 4\pi/\lambda \cdot \sin(\theta/2)$ , where  $\theta$  is the scattering angle and  $\lambda$  the wave length of electron. The prime summation indicates omission of terms for which  $i=j$  and both sums are carried out over all the atoms in the molecule. The term  $\cos [\eta_i(s) - \eta_j(s)]$  is the

phase factor arising from the difference in scattering amplitude between the waves scattered from  $i$  and  $j$  atoms. It may be neglected if the difference in atomic number between  $i$  and  $j$  atoms is less than ten, but it can not be neglected in the case of  $\text{SbF}_3$  because the difference is forty two.

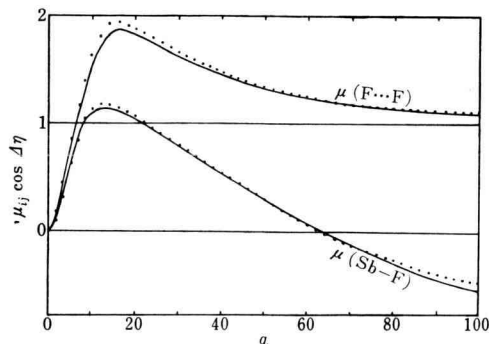


Fig. 3. Comparison of the values of  $\mu_{ij} \cos \Delta\eta$  calculated by Bonham-Ukaji's equation (full lines) and by Kimura-Konaka's (dotted lines).

Fig. 3 shows the theoretical background curves of the scattering intensities due to the interatomic distances of Sb-F and F...F, respectively. The cut-off point is found to be about 63 in  $q$ -values at the point of  $\cos [\Delta\eta_{\text{Sb-F}}(q)] = 0$ , i.e.,  $\Delta\eta = \pi/2$ , in which  $q = 10/\pi$  s. It agrees well with the calculated value of 62.5  $q$  by the equation of Bonham and Ukaji.<sup>3)</sup> The dotted curves in Fig. 3 represent the same theoretical curves by means of the recent calculation of the complex scattering factors extended to the atoms from Kr to Cm using the Thomas-Fermi-Dirac potentials by Kimura, Konaka and Ogasawara.<sup>4)</sup> These are very close to the curves of the full lines in Fig. 3, so the use of both methods are supposed to make no difference in the determination of the molecular structure of  $\text{SbF}_3$ .

**Least-squares Analysis.** The experimental

molecular intensities obtained from the six plates were analyzed by the standard least-squares method.<sup>20)</sup> The theoretical molecular intensity was calculated from the following equation, which was obtained from the Eq. (2) by changing the variable from  $s$  to  $q$  as,

$$qM(q) = k \sum'_{ij} A_{ij} \mu_{ij} \cos \Delta\eta_{ij} \exp \left[ -\frac{1}{2} \left( \frac{\pi}{10} q \right)^2 l_{ij}^2 \times \sin \left[ \frac{\pi}{10} q \left\{ r_{ij} - \left( \frac{\pi}{10} q \right)^2 \kappa_{ij} \right\} \right] \right] \quad (3)$$

where  $k$  is the index of resolution, and

$$A_{ij} = \frac{10}{\pi} \frac{1}{r_{a_{ij}}} \cdot \frac{Z_i \cdot Z_j}{\sum_k Z_k (Z_k - 1)},$$

$$\mu_{ij} = \frac{|F_i| |F_j|}{\sum_k F_k^2 + \sum_k S_k} \cdot \frac{\sum_k Z_k (Z_k - 1)}{Z_i Z_j}, \quad (4)$$

$$\kappa_{ij} = \frac{1}{6} a l^4 \left\{ 1 - \frac{8\varepsilon}{(1 + \varepsilon)^2} \right\},$$

$$\varepsilon = \exp \left( \frac{h\nu}{kT} \right), \quad (5)$$

and all the other notations have their usual significance. The final smooth background curves and the corresponding molecular intensity curves were determined, in accordance with the non-negativity criterion, by the Fourier inverse transformation of the radial distribution curves.<sup>21)</sup> The determinations by the least-squares method of the structure were carried out by curve-fitting the theoretical molecular intensity,  $qM(q)^{theo}$ , to the observed ones,  $qM(q)^{obs}$ , with a conventional weight function shown in Fig. 4. The parameters refined by the least-squares treatments were  $k$ ,  $r_a(\text{Sb-F})$ ,  $r_a(\text{F...F})$ , and their associated mean amplitudes. The anharmonicity constants,  $\kappa_{ij}$  were

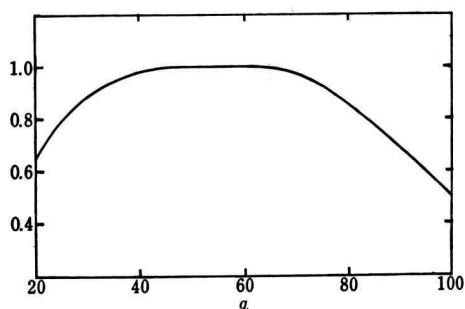


Fig. 4. The weight function for least-squares analysis.

calculated from the Eq. (5),<sup>22)</sup> assuming the Morse potential with the asymmetry constants,  $a$ , which has the dimension of  $\text{\AA}^{-1}$ .<sup>23)</sup> Although no appropriate method of the estimation of  $\kappa$ 's is available for non-bonded atom pairs, it was estimated to be one-third of the values from the Eq. (5) in the diatomic case suggested by Kuchitsu.<sup>24)</sup> An ambiguity in  $\kappa$ 's may be supposed to have no significant influence on the final structures in the present study.

The results of the least-squares adjustment for the six plates agreed well with one

another, as shown in Table I. The final values of the interatomic distance,  $r_g$ , which is the center of gravity of the radial distribution curve defined by the relation<sup>25)</sup>

$$r_g = r_a + l^2/r_a, \quad (6)$$

and the mean amplitudes are given in Table IV. The total limits of the error were estimated by following the procedure described in the previous paper.<sup>26)</sup>

## Results and Discussion

One of the radial distribution curves is shown in Fig. 2. The results of the least-squares analysis of molecular intensity curves,  $qM(q)$  are listed in Table I. It may be noted that the mean amplitudes derived from the plates analyzed are fairly in good agreement with one another in spite of the large deviations in the indices of resolution. A typical experimental molecular intensity curve is compared with the best-fit theoretical one in Fig. 2. The correction from  $r_a$  to  $r_g$  was 0.0030  $\text{\AA}$  and 0.020  $\text{\AA}$ , respectively, for the Sb-F and F...F distances,

Table I. Results of the least-square analysis of  $qM(q)$  of  $\text{SbF}_3$ . The figures in the brackets show the standard deviations.

Plate	$r_g$		$l_{ij}$		Index of resolution
	Sb-F	F...F	Sb-F	F...F	
1	1.8792 (0.0011)	2.7122 (0.0115)	0.0676 (0.0023)	0.1561 (0.0086)	0.894 (0.014)
2	1.8711 (0.0011)	2.8458 (0.0134)	0.0646 (0.0022)	0.1611 (0.0090)	0.863 (0.014)
3	1.8739 (0.0010)	2.7594 (0.0120)	0.0662 (0.0021)	0.1639 (0.0085)	0.904 (0.015)
4	1.8781 (0.0015)	2.7337 (0.0287)	0.0631 (0.0031)	0.1731 (0.0117)	0.841 (0.019)
5	1.8782 (0.0011)	2.7060 (0.0105)	0.0679 (0.0022)	0.1534 (0.0080)	0.999 (0.014)
6	1.8800 (0.0011)	2.6835 (0.0096)	0.0623 (0.0021)	0.1412 (0.0075)	0.949 (0.016)
Mean value*	1.8766 (0.0011)	2.7401 (0.0142)	0.0654 (0.0023)	0.1581 (0.0066)	0.908 (0.015)

\* The mean values are the simple arithmetic mean; the final results are obtained after the treatments of the random and systematic error corrections for each plate.

Table II. Errors in the interatomic distances.

Source of error	$r_g$ (Sb-F)	$r_g$ (F...F)
Random:		
2.5 $\sigma_1$	0.0023 A	0.0065 A
2.5 $\sigma_2$	0.0043	0.0068
Systematic:		
Systematic:	0.0033	0.0051
scale factor (0.13%)	0.0033	0.0051
weight	0.0055	0.0085
Limit of error	0.0055	0.0085

Table III. Errors in the mean amplitudes.

Source of error	$l$ (Sb-F)	$l$ (F...F)
Random:		
2.5 $\sigma_1$	0.0031 A	0.0058 A
2.5 $\sigma_2$	0.0045	0.0060
Systematic:		
sample size	0.0010	0.0012
weight	0.0029	0.0029
scattering factor	—	0.0018
extraneous scattering	0.0020	0.0015
	0.0005	—
Limit of error	0.0065	0.0102

respectively. The deviations of the most probable values of the bond length of the Sb-F and F...F are essentially negligible when the complex atomic scattering factor calculated by the method of Bonham and Ukaji<sup>9)</sup> is used in place of that calculated by the method of Kimura et. al.<sup>4)</sup> The estimates of the errors of the interatomic distances and the mean amplitudes are summarized in Tables II and III, respectively. The index of resolution was found to be  $0.84 \pm 0.20$ . The limit of error,  $\pm 0.20$ , was estimated from the random error of 0.14

( $2.5 \times \sigma_2$ ), plus the systematic error, 0.06, due to the uncertainties in the measurement of the nozzle temperature.

Table IV. Final results of the molecular parameters. (400°C)

	Sb-F (A)	F...F (A)
$r_a$	$1.873 \pm 0.005$	$2.72 \pm 0.03$
$r_g$	$1.876 \pm 0.005$	$2.74 \pm 0.04$
( $\angle$ FSbF)		$(94.5 \pm 1.8^\circ)$
$\ell$ (obs)	$0.066 \pm 0.007$	$0.16 \pm 0.03$
$\ell$ (calc)	0.068	0.150

Table V. Molecular structures of Group V trifluorides.

Molecule	X-F (A)	$\angle$ FXF ( $^\circ$ )
NF <sub>3</sub>	$1.365 \pm 0.002$	$102.37 \pm 0.04^a)$
PF <sub>3</sub>	$1.570 \pm 0.001$	$97.8 \pm 0.2^b)$
AsF <sub>3</sub>	$1.708_9 \pm 0.001_6$	$95.9 \pm 0.4^c)$
SbF <sub>3</sub>	$1.876 \pm 0.005$	$94.5 \pm 1.8^d)$
	$1.879 \pm 0.004$	$95.0 \pm 0.8^e)$

a) M. Otake, C. Matsumura and Y. Morino, J. Mol. Spectro., **28**, 316 (1968).

b) Ref. 6.

c) S. Konaka and M. Kimura, Bull. Chem. Soc. Japan, **43**, 1693 (1970).

d) Present work.

e) Ref. 2.

The final results of the molecular parameters are listed in Table IV. These completely agree with the proposal of Morino et. al.<sup>6)</sup> In Table V, the molecular structures of trifluorides of the series of elements of the Group V are cited for comparison.

The relation between the mean amplitudes and force constants of a  $XY_3$  type of molecule (e.g.,  $C_{3v}$  symmetry) has been discussed by Iwasaki and Hedberg<sup>27)</sup> for phosphorous trichloride. The general quadratic potential function of antimony trifluoride is described by a set of six force constants, for example, by  $F_{11}$ ,  $F_{12}$ ,  $F_{22}$  for  $A_1$  species;  $F_{33}$ ,  $F_{34}$ , and  $F_{44}$  for E species, in terms of the ordinary symmetry coordinates as defined

in the reference.<sup>28)</sup> They are related to the force constants in terms of the internal coordinates:

A<sub>1</sub>-species

$$\begin{aligned} F_{11} &= f_r + 2f_{rr}, \\ F_{12} &= 2f_{r\theta} + f_{r\theta'}, \\ F_{22} &= f_\theta + 2f_{\theta\theta'}; \end{aligned} \quad (7-a)$$

E-species

$$\begin{aligned} F_{33} &= f_r - f_{rr'}, \\ F_{34} &= f_r - f_{r\theta'}, \\ F_{44} &= f_\theta - f_{\theta\theta'}; \end{aligned} \quad (7-b)$$

where  $f_r$  and  $f_\theta$  are the stretching and bending force constants, respectively; and  $f_{rr'}$ ,  $f_{\theta\theta'}$ ,  $f_{r\theta'}$  and  $f_{r\theta}$  are the interaction constants corresponding to the neighboring bonds neighboring angles, neighboring bond and angle, and opposite bond and angle, respectively.

Table VI. Observed infrared spectra of SbF<sub>3</sub>\*  
(cm<sup>-1</sup>)

	(obs)	(calc)
<b>A<sub>1</sub> species</b>		
$\nu_1$	565	565.4
$\nu_2$	277	277.1
<b>E species</b>		
$\nu_3$	535	534.8
$\nu_4$	244	244.9

\* Partly presented by authors at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1969.

The four infrared frequencies, as in Table VI, combined with the two observed mean amplitudes, are sufficient for determining all the six of force constants. It is important to note that the values of the force constants are restricted by a set of relations realized by the four infrared frequencies. This is due to the requirement that force constants should be real quantities; this will

be shown below for the A<sub>1</sub> species. If the observed frequencies,  $\nu_1$  and  $\nu_2$ , are substituted into the secular equation,

$$|GF - \lambda_i E| = 0 \quad (8)$$

the following two equations will be obtained for the three force constants;

$$\begin{aligned} \lambda_1 + \lambda_2 &= G_{11}F_{11} + 2G_{12}F_{12} + G_{22}F_{22} \\ \lambda_1\lambda_2 &= (G_{11}G_{22} + G_{12}^2)(F_{11}F_{22} + F_{12}^2) \end{aligned} \quad (9)$$

where  $\lambda_i = (2\pi c \nu_i)^2$ . By eliminating one of the force constants, say,  $F_{22}$  from above equations, a quadratic equation for  $F_{11}$  and  $F_{12}$  is obtained. Then, from the requirement that  $F_{11}$  is real,  $F_{12}$  is limited to a range such that  $-0.20 < F_{12} < 0.20$  mdyn./Å. The values of  $F_{11}$  and  $F_{12}$  allowed were determined by the above ranges of the  $F_{12}$ . Fig. 5 shows this situation. A similar treatment was made in the case of the degenerate vibrational modes of the E-species.

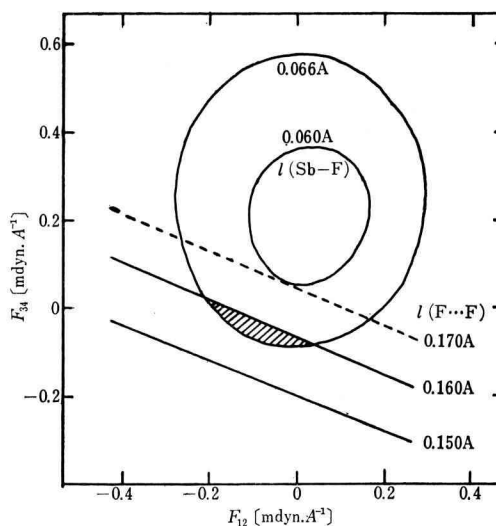


Fig. 5. Correlation curve of  $F_{34}$  versus  $F_{12}$  of SbF<sub>3</sub>.

Since the number of unknown force constants is six, correlation curves are obtain-

Table VII. Force constants in symmetry coordinates.

[mdyn·Å <sup>-1</sup> ]			
A <sub>1</sub> species		E species	
<b>F<sub>11</sub></b>	<b>3.05±0.05</b>	<b>F<sub>33</sub></b>	<b>2.74±0.07</b>
<b>F<sub>12</sub></b>	<b>-0.11±0.09</b>	<b>F<sub>34</sub></b>	<b>-0.03±0.06</b>
<b>F<sub>22</sub></b>	<b>0.36±0.08</b>	<b>F<sub>44</sub></b>	<b>0.29±0.09</b>

ed on the plane for  $F_{12}$  and  $F_{34}$  from the four frequencies and one mean amplitude. Another set of four frequencies and two mean amplitude give the other correlation. Thus the force constants can be determined as the crossing on the real plane of Fig. 5, but the hatched area shows the probable values of the force constants given from the mean amplitudes which are compatible with the infrared spectra in the same figure. The values of  $F_{12}$  and  $F_{34}$  obtained are  $-0.12 \pm 0.08$  and  $-0.03 \pm 0.05$  mdyn./Å, respectively. The six force constants were subsequently determined. The final values obtained are listed in Table VII. It is apparent that these values are reasonable when compared with those of the trifluorides of the series of elements of the Group V, e.g.,  $\text{NF}_3$ ,  $\text{PF}_3$ , and  $\text{AsF}_3$ .<sup>29)</sup>

We would like to thank Prof. K. Kuchitsu and his research members for their helpful discussions. Our thanks are also due to the Computer Center of the University of Tokyo for services.

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